

RADIOMETRIC CLOCKS

This paper provides an introduction to radioactivity, and how geologists exploit radioactive decay to determine the age of rocks.

Introduction

In the present nuclear age, the devastating effects of radioactivity have been highlighted by such issues as nuclear weapons testing and radioactive waste disposal, and by the reactor incidents at Three Mile Island and Chernobyl. These events illustrate the vexing problems that can be associated with high levels of radioactivity. However, the presence of radioactivity is not limited to nuclear reactors and atom bombs. We are constantly being showered by very low levels of *background radioactivity*, which originates from many different sources, some familiar, others distant. A variety of building materials, including cement and rocks, are sources of low-level radioactivity. Certain soil types contain small amounts of radioactive substances. Radioactive Carbon-14 is present in most plants and animals (including our own bodies). Even the air all around us contains a very small proportion of radioactive gasses, like Radon, which has recently become a controversial topic. Cosmic rays, which originate in outer space, also contribute to the background radioactivity. These rays are constantly bombarding the outer atmosphere, crashing into the gas molecules there and creating a mist of secondary radioactivity that reaches the Earth's surface. The cumulative effect of all of these sources results in a continuous shower of low-level radioactivity, referred to as background radioactivity.

In addition to these environmental sources of radioactivity, many other localized, man-made sources commonly exist around the home and in the workplace. Many smoke detectors contain radioactive Americium-241. The paint used for the numbers and hands of some old watches and clocks contains radioactive Radium salts. Some other very old paints, used on such items as chinaware, contain Uranium salts. Many radioactive isotopes are also used in medicine, such as radioactive Iodine-129 and Cesium-137. These radioactive sources are local, and are well understood. If handled with care, they do not pose the same dangers as high levels of radioactivity, such as are found in association with nuclear weapons fuel, as well as near the damaged reactor at Chernobyl. This paper seeks to provide some background about the nature of radioactivity, and to present at least one way that people have learned to exploit radioactivity to learn more about the world we live in: radiometric dating of rocks.

Chemical elements are often displayed the ‘Periodic Table of the Elements’ (shown below), which primarily arranges the display of elements according to the number of protons in the nucleus.

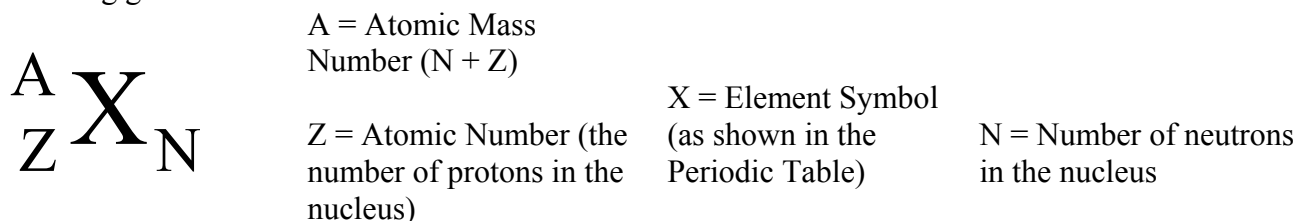
hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
cesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 ★		lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]				
francium 87 Fr [223]	radium 88 Ra [226]	89-102 ★ ★		lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	unnilium 110 Uun [271]	ununium 111 Uuu [272]	unbibium 112 Uub [277]	ununquadium 114 Uuq [289]									

* Lanthanide series

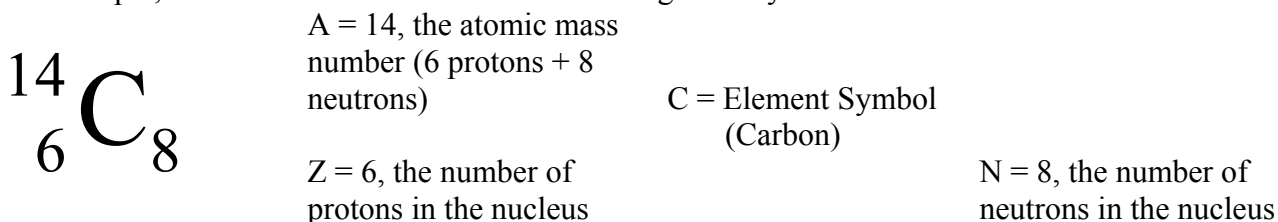
lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

** Actinide series

In the Periodic Table, the elements are also arranged into groups based on their chemical properties. Each atom of a given element contains a fixed number of protons inside the nucleus, and an equal number of electrons orbiting the nucleus. The number of protons in the nucleus is known as the Atomic Number, and is usually denoted by Z . In addition to protons, the nucleus of every element also contains neutrons. Atoms of the same element always have the same number of protons, but they can have a different number of neutrons in the nucleus. Two atoms of the same element that have a different number of neutrons are called isotopes of that element. The number of neutrons in the nucleus of an atom is usually denoted by N . In general terminology, an atom with atomic number Z and neutron number N is known as a **nuclide**. The total number of protons plus neutrons is known as the mass number of a nuclide, and is usually denoted by A . Any nuclide can be specified as shown in the following generalized notation:



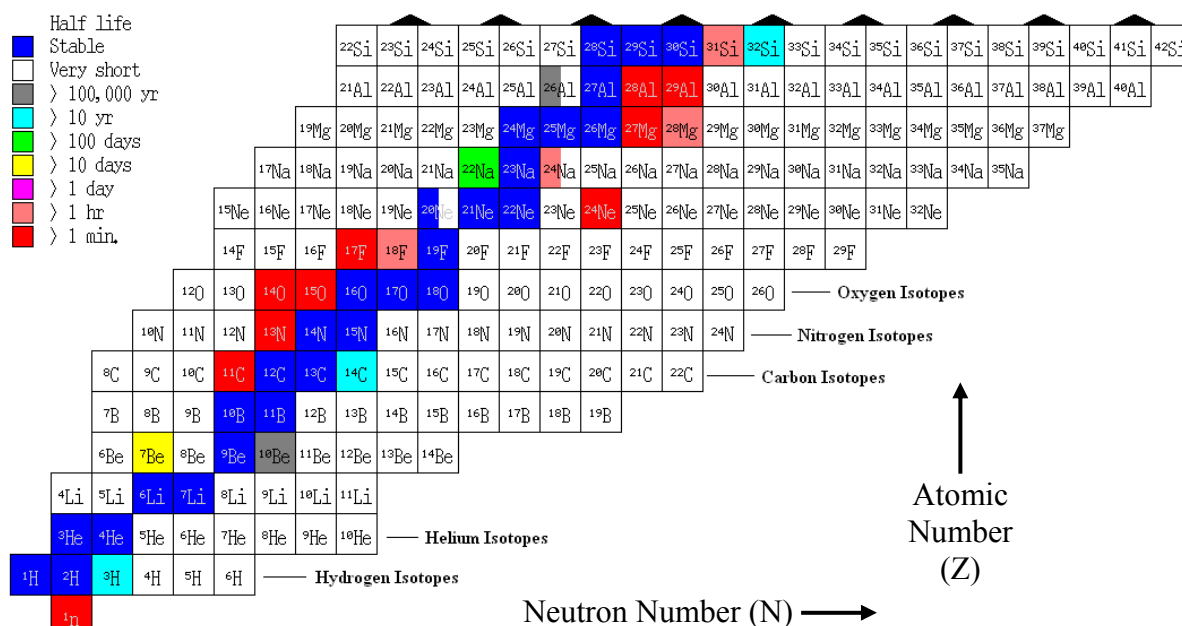
For example, the nuclide called “Carbon-14” is designated by:



The general notation here is somewhat redundant, and several shorthand variations are frequently used. For instance, “Carbon-14” denotes a carbon atom with atomic mass number 14. Since it is commonly known (from the Periodic Table, for instance) that all carbon atoms have 6 protons, it can be deduced that Carbon-14 has 8 neutrons (14 minus 6 equals 8). Carbon-14 is also frequently written ^{14}C , omitting the atomic number (6) and neutron number (8) displayed in the most general notation.

Chart of the Nuclides

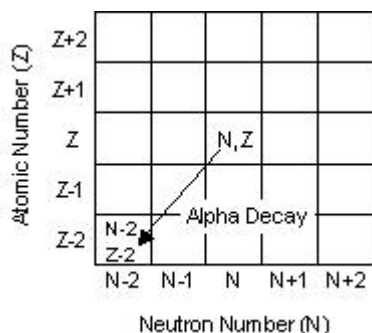
Every element in the Periodic Table has several isotopes, determined by the number of neutrons in the nucleus. It would be somewhat difficult to display all the isotopes of every element in the format of the Periodic Table. The “Chart of the Nuclides” aims to display all of the known isotopes for every element in the Periodic Table, at the expense of chemically similar groupings used by the Periodic Table. The image below is a small portion of the entire Chart of the Nuclides, showing known isotopes of the elements Hydrogen through Silicon.



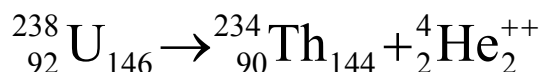
Radioactive Decay

The forces holding the nucleus of an atom together are very strong, and the nucleus is packed very tightly with protons and neutrons. About 10% of all nuclides have a stable nucleus, meaning that the configuration of protons and neutrons in the nucleus will persist indefinitely under normal conditions. In general, however, the nuclei of most atoms are not stable. This means that, even under normal conditions, the nucleus of an unstable atom will have some propensity to ‘decay’ spontaneously and become rearranged into another configuration. These unstable isotopes are known as *radionuclides*, or *radioactive nuclides*, or *radioactive isotopes*. The process whereby a nucleus is rearranged is called nuclear decay, or radioactive decay. Energy is also released during a nuclear decay, in the form of particles or waves, or both. The term ‘radioactive’ is a reference to the energy released during the spontaneous rearrangement of an atom’s nucleus. There are several ways that an unstable nucleus can be spontaneously rearranged as a result of radioactive decay. The main radioactive decay modes are listed below.

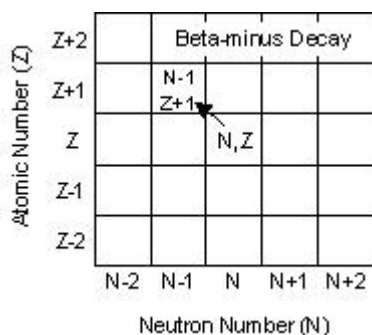
Alpha (α) decay. In alpha decay, the unstable “parent” nuclide emits a single particle consisting of two protons and two neutrons. This ejected particle is called an alpha particle (α -particle). An alpha particle is identical to a Helium-4 nucleus (without the orbiting electrons). With this decay mode, the atomic number (Z) of the resulting “daughter” nuclide is two units lower than the parent, because the parent lost two protons. The atomic mass number of the daughter is four units less than the parent. In most alpha decays, the daughter nucleus will also emit a gamma ray (γ -ray) as the nucleus settles into its ground state. The emitted alpha particle contains kinetic energy (motion energy), which is converted into heat as the emitted particle interacts with surrounding atoms.



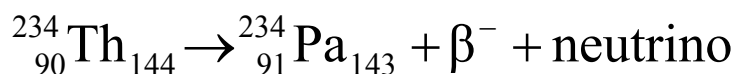
Example of α decay:



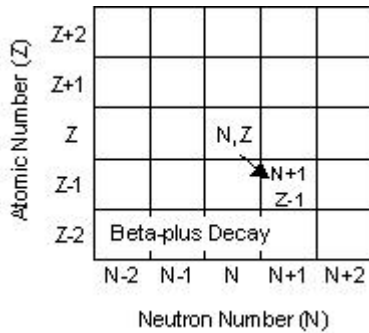
Beta-minus (β^-) Decay. Beta-minus decay (also called negatron decay) often occurs when there is an ‘excess’ of neutrons in the nucleus. A neutron is spontaneously converted into a proton, which is accompanied by the emission of a beta particle and an anti-neutrino (the anti-matter counterpart of a neutrino). In beta-minus decay, the beta particle is identical to an electron. In this decay mode, the atomic mass of the parent does not change, because the mass of an electron and the mass of a neutrino are negligible. The atomic number of the resulting daughter nuclide is one more than the atomic number of the parent nuclide, because there is one more proton in the nucleus than there was before the decay. The neutron number of the parent nuclide is reduced by one unit in the daughter nuclide.



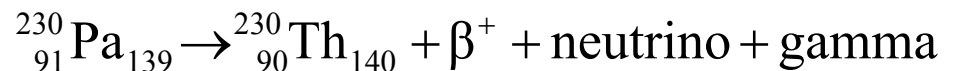
Example of β^- decay:



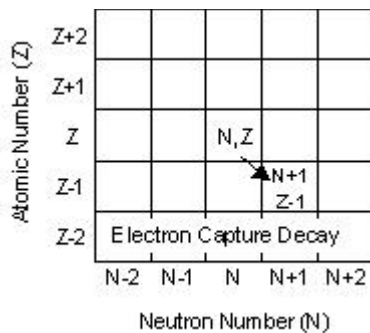
Beta-plus (β^+) Decay. Beta-plus decay (also called positron decay), usually occurs when there is a 'deficiency' of neutrons in the nucleus. A proton is spontaneously converted to a neutron, which is accompanied by the emission of a positron (β^+ , the anti-matter counterpart of an electron) and a neutrino. The positron will eventually annihilate with an electron, producing two gamma rays. The daughter nuclide will also emit a gamma ray (γ -ray) as the nucleus settles into its ground state. As in beta-minus decay, the mass of the daughter nuclide is the same as the parent. But in beta-plus decay, the atomic number decreases by one and the neutron number increases by one.



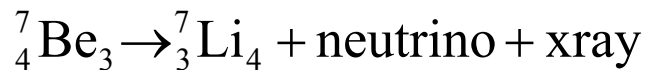
Example of β^+ decay:



Electron Capture Decay. This is similar to β^+ decay, except that the nucleus captures an extra-nuclear electron. A proton is converted to a neutron, which is accompanied by the emission of a neutrino. The daughter nuclide will also emit an x-ray as other electrons fill the void in the orbit where the captured electron came from. As in beta-plus decay, the mass of the daughter nuclide is the same as the parent, and the atomic number decreases by one while the neutron number increases by one.



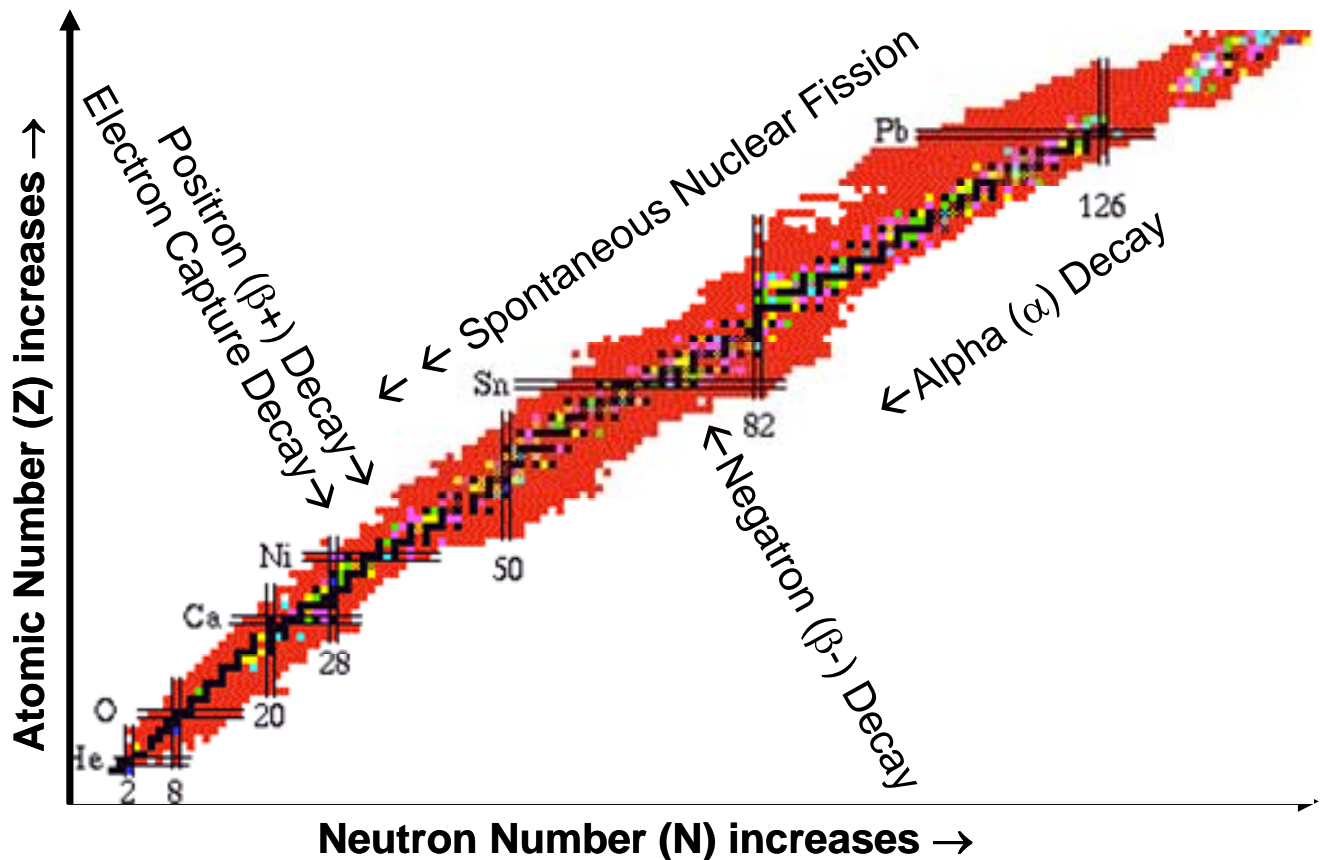
Example of electron capture decay:



Spontaneous Nuclear Fission. Some nuclides of heavy elements such as U, Pu, Am, Np, Cm, Fm can undergo radioactive decay by spontaneous fission. In this process, the nucleus splits into two large fragments, and neutrons, α -particles and other particles and energy are liberated. The fission product nuclides have large kinetic energy, and fly apart at nearly 180° from each other. The daughter nuclides typically have an excess of neutrons, and thus decay by emitting β^- particles and gamma rays until a stable nuclide is produced.

Example of spontaneous nuclear fission:





Most of the stable isotopes in the Chart of the Nuclides lie along the “main diagonal”. Isotopes along the “main diagonal” have approximately the same number of neutrons and protons in the nucleus. Additionally, isotopes with larger nuclei tend to be less stable than isotopes with smaller nuclei. Each of the radioactive decay modes transforms a “parent” isotope in such a way that the “daughter” isotope moves toward a more stable form:

Positron (β^+) Decay, and **Electron Capture Decay**, usually occur when there is a ‘deficiency’ of neutrons in the nucleus. This means that there are more protons than in the nucleus, placing the isotope above the “main diagonal”. These decay modes reduce the number of Protons and increase the number of Neutrons, so the “daughter” isotope is closer to the “main diagonal” than the “parent isotope”.

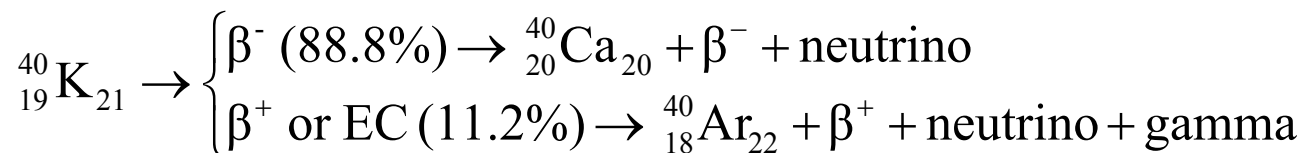
Negatron (β^-) Decay usually occurs when there is an ‘excess’ of neutrons in the nucleus. This means that there are fewer protons than neutrons in the nucleus, placing the isotope below the “main diagonal”. Negatron decay increases the number of Protons and decreases the number of Neutrons, so the “daughter” isotope is closer to the “main diagonal” than the “parent isotope”.

Alpha (α) Decay reduces the number of Protons the number of Neutrons by the same amount, moving the “parent” isotope *along* the “main diagonal” to produce a “daughter” isotope that has a smaller nucleus than the “parent” isotope.

Spontaneous Nuclear Fission only occurs in heavy isotopes, *i.e.*, isotopes with large nuclei. This decay mode produces two (or more) “daughter” isotopes that have much smaller nuclei than the “parent” isotope.

Branched Decay. Some nuclides may undergo more than one type of decay. For example, one atom of a particular nuclide may undergo β^- decay, while another atom of the same nuclide may undergo β^+ decay. Typically, a constant proportion of atoms will undergo each type of decay.

Example of branched decay:



Decay Series. Some heavy radionuclides decay into daughter products that are themselves unstable, giving rise to a series of decay products. The following table shows the complete decay series for Uranium-238. The ultimate stable daughter nuclide is ${}^{206}\text{Pb}$ (lead).

NUCLIDE	DECAY MODE	HALF LIFE	Decay Energy (MeV)	PRODUCT OF DECAY
${}^{238}\text{U}$	α	$4.468 \cdot 10^9 \text{ a}$	4.27	${}^{234}\text{Th}$
${}^{234}\text{Th}$	β^-	24.10 d	0.273	${}^{234}\text{Pa}$
${}^{234}\text{Pa}$	β^-	6.70 h	2.197	${}^{234}\text{U}$
${}^{234}\text{U}$	α	245500 a	4.859	${}^{230}\text{Th}$
${}^{230}\text{Th}$	α	75380 a	4.77	${}^{226}\text{Ra}$
${}^{226}\text{Ra}$	α	1602 a	4.871	${}^{222}\text{Rn}$
${}^{222}\text{Rn}$	α	3.8235 d	5.59	${}^{218}\text{Po}$
${}^{218}\text{Po}$	α 99.98 %	3.10 min	6.615	${}^{214}\text{Pb}$
	β^- 0.02 %		0.265	${}^{218}\text{At}$
${}^{218}\text{At}$	α 99.90 %	1.5 s	6.874	${}^{214}\text{Bi}$
	β^- 0.10 %		2.883	${}^{218}\text{Rn}$
${}^{218}\text{Rn}$	α	35 ms	7.263	${}^{214}\text{Po}$
${}^{214}\text{Pb}$	β^-	26.8 min	1.024	${}^{214}\text{Bi}$
${}^{214}\text{Bi}$	β^- 99.98 %	19.9 min	3.272	${}^{214}\text{Po}$
	α 0.02 %		5.617	${}^{210}\text{Tl}$
${}^{214}\text{Po}$	α	0.1643 ms	7.883	${}^{210}\text{Pb}$
${}^{210}\text{Tl}$	β^-	1.30 min	5.484	${}^{210}\text{Pb}$
${}^{210}\text{Pb}$	β^-	22.3 a	0.064	${}^{210}\text{Bi}$
${}^{210}\text{Bi}$	β^- 99.99987%	5.013 d	1.426	${}^{210}\text{Po}$
	α 0.00013%		5.982	${}^{206}\text{Tl}$
${}^{210}\text{Po}$	α	138.376 d	5.407	${}^{206}\text{Pb}$
${}^{206}\text{Tl}$	β^-	4.199 min	1.533	${}^{206}\text{Pb}$
${}^{206}\text{Pb}$	--	stable	--	--

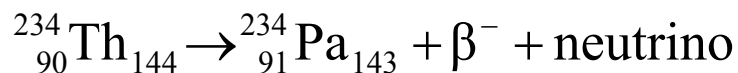
Half-Life

The atomic nuclei of radioactive elements are “unstable.” As stated previously, this means that even under normal conditions, the nucleus of an unstable atom will have some propensity to ‘decay’ spontaneously into another element. The lifetime of any single atom of a radioactive element is *indeterminate*, and depends on the relative stability of the nuclear configuration. Some nuclei are highly unstable; in this case, the lifetime of any single atom is indeterminate but relatively short. Some nuclear configurations are only slightly unstable, and the lifetime of any single atom is indeterminate but relatively long. Even though the lifetime of any single unstable atom is indeterminate, when a large number of atoms of the same radionuclide are considered as a group, *the decay process of the group of atoms follows a very regular pattern*. If a group of atoms of the same type of radionuclide is monitored over time, not all of the atoms in the group will decay at the same time. Rather, the number of atoms in the group that will decay at any given point in time is **proportional to the total number of atoms in the group at that time**. Initially, the number of decays is relatively ‘high’ (because the group is ‘large’). But as time progresses, the atoms that have already decayed are no longer in the group (because they are no longer the same type of nuclide). So, the original group has become smaller; and if the number of decays remains proportional to the number of atoms in the group, then the number of decays will decrease, along with the size of the group. All known radionuclides have been shown, through experimental evidence, to follow this pattern. Nuclides that are highly unstable have large proportionality factors; nuclides with more slight instability have smaller proportionality factors. The size of the proportionality factor is inherent to each radionuclide.

The pattern whereby the number of decays at any given time is proportional to the number of atoms in the group at that time can be described mathematically as *exponential decay*. One of the characteristics of exponential decay is that the average amount of time required for the size of the group to be reduced by half is *constant*. It does not matter how many atoms are in the group; it takes approximately the same amount of time for 1,000 atoms to decay to 500 as it takes for 1,000,000 to decay to 500,000. This is the concept of *half-life*.

The half-life of a radioactive nuclide is defined to be the average amount of time required for half of the number of atoms in a group to decay. The half-lives for different nuclides range from fractions of a second to billions of years. Stable nuclides, since they do not decay, do not have a half-life.

For example, consider the β^- decay of ^{234}Th to ^{234}Pa .



In the table above, the half-life of ^{234}Th is listed as 24.10 days, which has been determined experimentally. Based on this number, if 100 grams of ^{234}Th are originally present, then after 24.10 days, approximately 50 grams of ^{234}Th will remain (and 50 grams of ^{234}Pa will have been created). After 48.20 days (two half-lives), approximately 25 grams of ^{234}Th will remain. After 72.3 days (three half-lives), approximately 12.5 grams of ^{234}Th will remain; and so on. Although the decay of individual atoms is random and cannot be predicted, the half-life of a large number of atoms in a group is very accurate and predictable. The decay rate of a radionuclide is a characteristic of that nuclide and is not affected by any change in environmental (physical or chemical) conditions (induced fission is the only known exception).

Whenever the number of atoms in a group that will decay at any given point in time is proportional to the total number of atoms in the group at that time, the decay mode follows an **exponential decay curve**. As a radioactive isotope decays, the amount of the radioactive “parent” isotope will decrease over time, according to its exponential decay curve:

$$A(t) = A(0) \cdot e^{-k \cdot t}$$

where t is given in years from the time the radioactive substance was formed; $A(t)$ is the amount of “parent” isotope present at time t ; $A(0)$ is the initial amount of “parent” isotope present; and k is a decay constant specific to each isotope.

If the half-life of a substance is known, for instance from some measurement, then the decay constant can be found from the equation

$$k = \frac{\ln(2)}{\text{half life (years)}} \quad \text{note: this is found from solving } \frac{A(t)}{A(0)} = e^{-k \cdot t} = 0.5 \Rightarrow \ln(e^{-k \cdot t}) = \ln(0.5)$$

Radioactive ^{14}C has a half-life of 5730 years. So, the decay constant for ^{14}C is:

$$k = \frac{\ln(2)}{5730 \text{ years}} = 1.20968 \cdot 10^{-4}$$

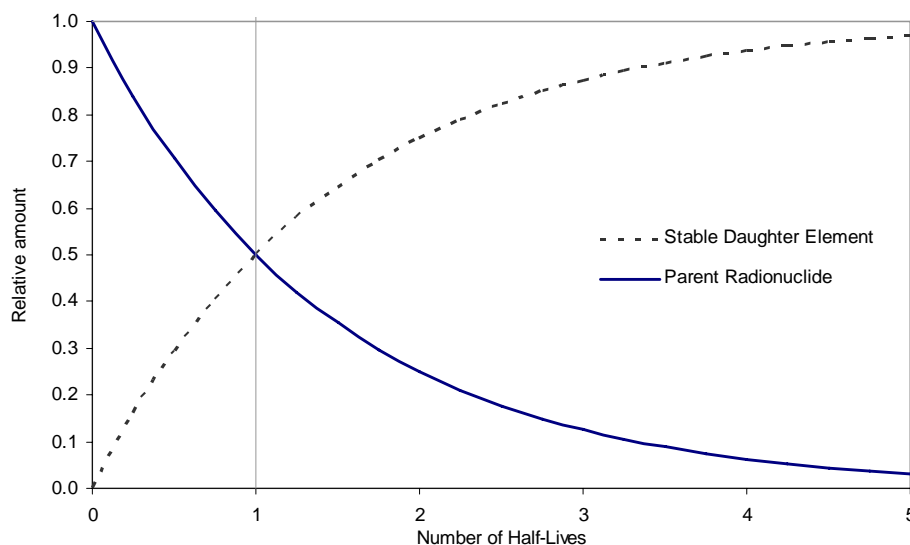
For Geologists, a more convenient form of the exponential decay equation gives the *relative amount* of parent isotope present at any time t :

$$\frac{A(t)}{A(0)} = e^{-k \cdot t}$$

This is more convenient, because the value of $A(0)$ is rarely, if ever, a known quantity. If a time in years is input into this function, the output of the function will be the *fraction* of “parent” isotope remaining at that time. This “relative amount” decay curve will always start at 100%, because the fraction of “parent” isotope remaining at the outset is always 1. The key for Geologists is that, as the “parent” isotope decays, the decay produces a “daughter” isotope. If the “daughter” isotope is stable, then the relative amount of “daughter” isotope created by radioactive decay of the “parent” isotope will also follow an exponential curve:

$$\frac{D(t)}{A(0)} = 1 - e^{-k \cdot t} \quad \text{where } D(t) \text{ is the amount of stable “daughter” element present at time } t$$

As each atom of a “parent” isotope decays, the decay produces one atom of stable “daughter” element. This relationship is shown in the graph below.

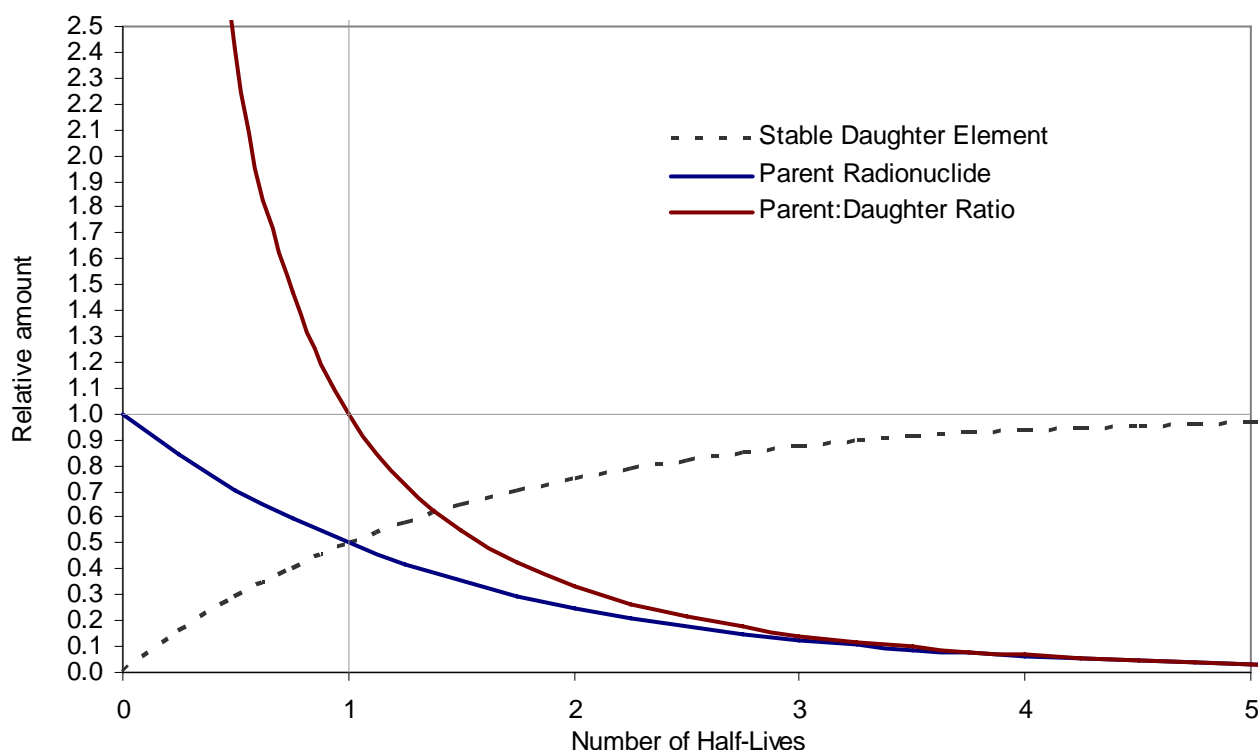


Radiometric ‘Clocks’

The characteristic decay rates of radionuclides, along with the apparent imperviousness of decay to environmental conditions, make naturally occurring radionuclides suitable for use as a kind of ‘clock’ in certain types of geological materials. Consider the decay of a parent radionuclide into a single stable daughter element. As the parent radionuclide decays, the amount of daughter element builds up, according to the characteristics of exponential decay. Based on the equations for exponential decay, the ratio of “parent” to “daughter” isotopes is

$$\frac{\left(\frac{A(t)}{A(0)}\right)}{\left(\frac{D(t)}{A(0)}\right)} = \frac{e^{-k \cdot t}}{1 - e^{-k \cdot t}} \Rightarrow \frac{A(t)}{D(t)} = \frac{e^{-k \cdot t}}{1 - e^{-k \cdot t}}$$

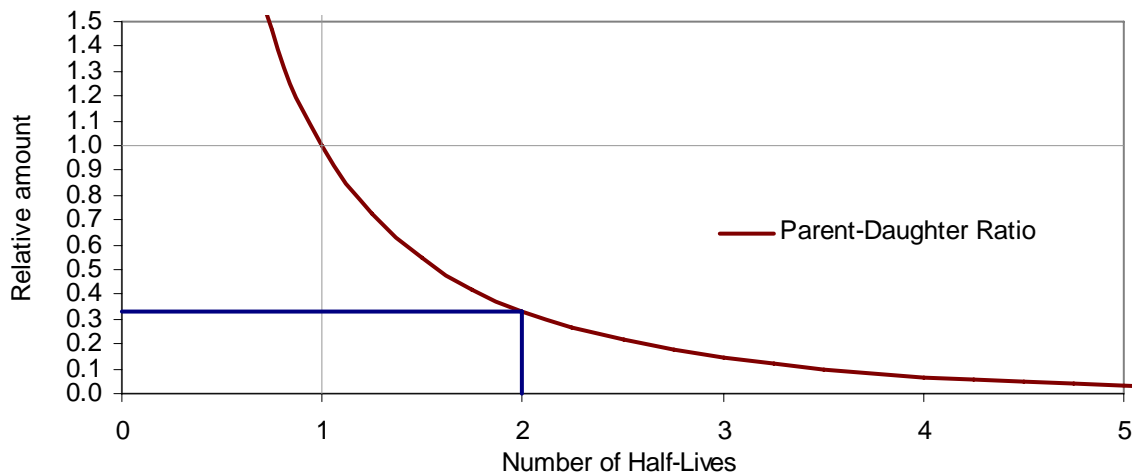
This situation is shown in the graph below.



The ratio of radioactive “parent” isotope to stable “daughter” isotope is something that can be measured (*e.g.*, in a mass spectrometer). Thus, the number of half-lives that have passed since the daughter began to accumulate can be determined from the graph. For example, if measurements indicate that there are equal amounts of the parent radionuclide and daughter element, then the parent:daughter ratio is 1.0, which corresponds to exactly one half-life, as shown in the graph above. Using the graph, any parent-daughter ratio can yield a half-life number. By also knowing the characteristic half-life of the parent radionuclide, the actual amount of time can be determined.

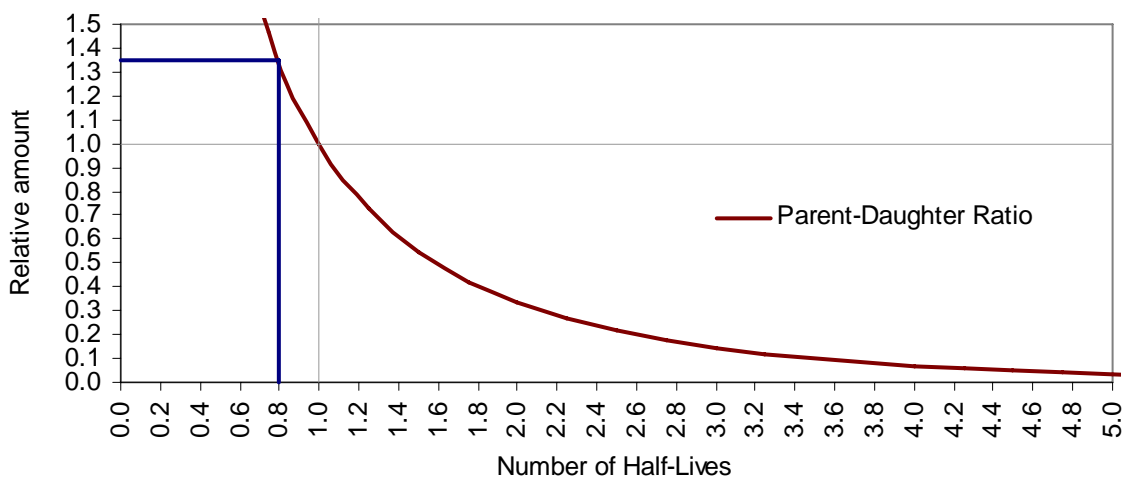
Here are a couple of examples:

1. If measurements determine that there is three times more of the daughter element present than there is of the parent radionuclide, then the parent:daughter ratio is $1/3 = 0.333$. The graph below indicates that a parent:daughter ratio of 0.333 corresponds to the point where exactly two half-lives have passed since the daughter element began accumulating.



If the “parent” isotope is ^{40}K , with a half-life of 1.3 billion years, then the amount of time that has passed since the daughter element began accumulating is $2 \cdot 1.3\text{Ga} = 2.6\text{Ga}$.

2. Suppose measurements determine that the parent:daughter ratio is 1.35. The graph below indicates that this parent:daughter ratio corresponds to the point where approximately 0.8 half-lives have passed since the daughter element began accumulating.



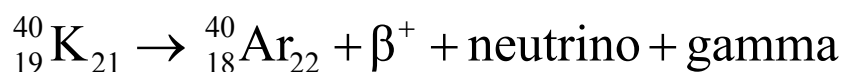
If the “parent” isotope in this case is ^{14}C , with a half-life of 5730 years, then the amount of time that has passed since the daughter element began accumulating is $0.8 \cdot 5730 \text{ years} = 4584 \text{ years}$.

Source of Radiometric Isotopes

There are four general categories of radioactive elements:

1. Naturally occurring (long-lived) radioactive elements that were present during the formation of the solar system. Examples (with half-lives): ^{238}U (4.5Ga), ^{235}U (0.7Ga), ^{232}Th (14Ga), ^{87}Rb (48.8Ga), and ^{40}K (1.3Ga) (1Ga is one Giga Anna, or one billion years).
2. Elements produced by the decay of the long-lived naturally occurring radioactive elements. Examples: ^{234}U , ^{230}Th , ^{226}Ra (see the Uranium decay series table above).
3. Elements produced by nuclear reactions occurring in nature (cosmogenic radionuclides). Examples: ^{14}C (5730 years), ^{10}Be (1.5Ma), ^{32}Si (276 years).
4. Artificially produced radioactive elements, i.e., radionuclides that can now be found in nature but were produced in nuclear reactors or nuclear explosions.

Some of these radionuclides become incorporated into the crystal lattices of minerals and rocks. For example, the mineral Microcline (“Potassium Feldspar”, or K-Spar) contains Potassium. Some of that Potassium will be radioactive ^{40}K , which has a half-life of 1.3 billion years. As shown above, 11.2% of the ^{40}K present in any sample of Microcline will undergo β^+ decay or electron capture to produce ^{40}Ar , which is a stable element.



The ^{40}K that decays to ^{40}Ar in a Microcline crystal lattice forms the basis of a radiometric clock as described above. When the Microcline crystal formed, it did not contain any traces of ^{40}Ar (this element is an inert gas, and does not form chemical bonds with mineral-forming elements). As the ^{40}K decays, the amount of ^{40}Ar builds up in the mineral lattice according to the exponential decay process. By measuring the relative amount of ^{40}K and ^{40}Ar in the mineral sample, the time from the formation of the crystal can be determined from the half-life of ^{40}K . This K-Ar ‘dating’ technique is the most common geochronometer used today. Modifications to the K-Ar technique have improved the accuracy of the original process. Due to the long half-life of ^{40}K , ‘young’ geological materials cannot be dated by K-Ar, because not enough time has passed for measurable amounts of ^{40}Ar to accumulate. For very young organic materials (<50,000 years), ^{14}C can be used (described in an additional handout).

The time that has passed since the daughter element began accumulating can be found algebraically as well as graphically:

$$\begin{aligned}\frac{A(t)}{D(t)} &= \frac{e^{-k \cdot t}}{1 - e^{-k \cdot t}} = x \quad (\text{solve for } x) \\ e^{-k \cdot t} &= x \cdot (1 - e^{-k \cdot t}) \Rightarrow e^{-k \cdot t} = x - x \cdot e^{-k \cdot t} \Rightarrow e^{-k \cdot t} + x \cdot e^{-k \cdot t} = x \Rightarrow e^{-k \cdot t} \cdot (1 + x) = x \\ e^{-k \cdot t} &= \frac{x}{(1 + x)} \Rightarrow \ln(e^{-k \cdot t}) = \ln\left(\frac{x}{(1 + x)}\right) \Rightarrow -k \cdot t = \ln\left(\frac{x}{(1 + x)}\right) \\ \Rightarrow t &= \left(\frac{-1}{k}\right) \cdot \ln\left(\frac{x}{(1 + x)}\right)\end{aligned}$$

MEASURING RADIOACTIVITY

The nature of radioactivity. Radioactivity is not unlike a watermelon seed being squeezed out from between one's fingertips and shot across the room. Radioactivity occurs when small particles are spontaneously emitted at high speeds from inside the nuclei of unstable atoms. The instability in the nucleus of a radioactive atom results from either a deficiency or an excess of neutrons, creating an incompatible environment for the existing configuration of particles in the nucleus. In general, this radioactive emission changes the original nucleus to form a new substance of increased stability. The particles that are emitted have sufficient energy to ionize gases in the environment; that is, when a particle from a radioactive nucleus is emitted, it flies outward through any surrounding material, and it travels with enough energy to dislodge electrons from atoms in the surrounding material, creating charged atoms (ions). The effects of such ionizing radiation have been exploited in the design of devices used to measure radioactivity levels, such as the Geiger counter.

During Alpha Decay, the nucleus of an unstable element emits a large, positively charged particle consisting of two protons and two neutrons (which is just a Helium nucleus). Due to their 'large' mass and positive charge, these particles are usually stopped before they travel through a few centimeters of air, and can even be stopped by a sheet of paper. The Thorium found in some lantern mantles and the Americium-241 present in many smoke detectors are both alpha emitters. During Beta Decay, small, negatively charged beta particles (also called nuclear electrons) are emitted. Since these particles have much smaller mass than the Helium nuclei of alpha decay, they can penetrate material to greater depths. Normally, a few millimeters of aluminum will stop beta particles. The Carbon-14 present in most plants and animals goes through the beta decay process, and subsequently forms Nitrogen. During Spontaneous Nuclear Fission, the nucleus of an unstable atom actually breaks into two fragments of unequal weight, creating two new atoms called fission-product nuclides. In the process of splitting apart, the nucleus will emit beta particles and gamma rays. The resulting fission-product nuclides are also usually unstable, and are therefore radioactive themselves. The gamma rays produced by fission are pulses of high-energy electromagnetic energy (photons), similar to very high-energy X-rays. Gamma rays are far more energetic than either alpha or beta particles, and can penetrate very deeply into most substances. Gamma rays can usually be stopped by a shield of Lead approximately 15 cm thick. The Uranium salts found in some older paints undergo spontaneous nuclear fission. Thorium-232 decays through spontaneous nuclear fission to produce Thoron gas in the atmosphere, just as Radium decays to Radon gas.

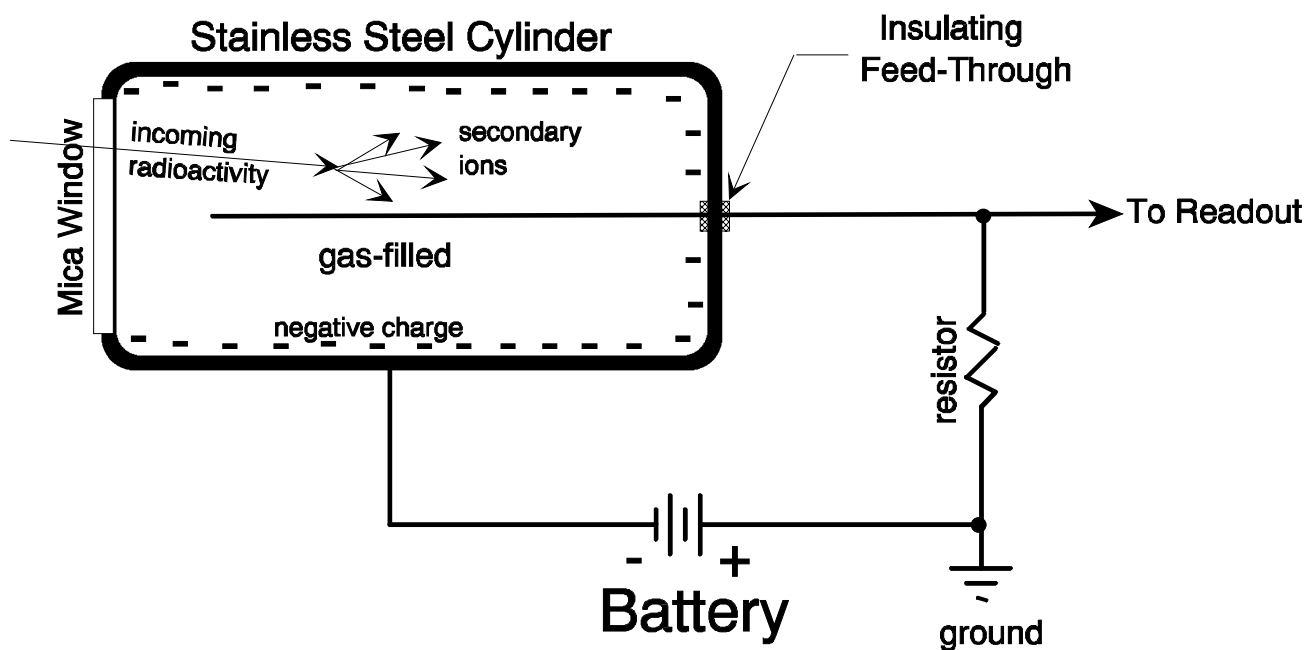
Units of Radioactivity. The alpha and beta particles and gamma rays, which are emitted by radioactive elements, are traveling at very high velocities. As they move through space, these particles travel by other molecules in the air and in solid substances. Eventually, they might run into another molecule, and the resulting collision would transfer some energy from the particle to the target molecule. In other cases, the particle might travel very close to a molecule; close enough to disrupt the electrons in the molecule's outer shell. These interactions often result in secondary *ionization*, which is the formation of charged particles. It follows that, as the number of particles which are present due to radioactivity increases, the amount of ionization will increase proportionately. One method of measuring radioactivity exploits this secondary ionization effect whereby the amount of radioactivity is determined from the amount of ionization present. One set of units used to describe radioactivity is actually based on the amount of ionization present. This can be seen in the following definition:

One **Röntgen** (sometimes spelled **Roentgen**) is that *quantity of radioactivity which produces 1.61×10^{12} ion pairs per gram of air*, which is equivalent to the number of ions which carry one electrostatic unit of charge in one cubic centimeter of air (at a specific temperature and pressure).

One **milli-Röntgen** (abbreviated mR) is equivalent to 1×10^{-3} Röntgen

One **micro-Röntgen** (abbreviated μR) is equivalent to 1×10^{-6} Röntgen

Measuring the presence of radioactivity with a Geiger Counter. From the preceding discussion, it is clear that there is radioactivity all around us. That is to say, there is a variety of very small particles flying around the room at very high velocities all the time. One method of measuring radioactivity is with a *Geiger counter*, which actually measures the amount of associated ionization. A Geiger counter consists of a gas-filled steel shell, which has an insulated metal wire mounted inside (see the diagram below). The front end of the cylinder consists of a thin mica cover, which allows a window for incoming particles emitted by radioactive substances. A battery is connected to the steel cylinder, applying a negative voltage to the cover. When a particle enters through the window, some of the gas inside the chamber is ionized, i.e., charged particles are created by the interaction between the high-velocity particle and the molecules of gas inside the chamber. The negative ions are repelled away from the walls of the chamber due to the negative charge there (like charges repel each other). These negative ions are readily conducted away from the negatively charged cylinder through the central wire. These ions then become a current in the wire. As this current passes through the resistor and toward ground, a voltage is developed at the top of the resistor. This voltage is then indicated on some type of readout scale. The Geiger counter does not differentiate between the different types of incoming radioactivity. Since alpha, beta and gamma radioactivity will all produce secondary ionization when they enter the gas-filled cylinder, the Geiger counter will produce the same indication regardless of the type of incoming radioactivity. The readouts of most Geiger counters indicate the *rate* at which the radioactivity is entering the cylinder, and are thus calibrated in milli-Röntgen/hour or micro-Röntgen/hour. That is, the Geiger counter indicates the amount of radioactivity (in Röntgen) *per unit of time* entering the chamber. Most Geiger counters also produce an audible click along with a visual readout for each ionization event.



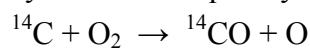
Some background information about ^{14}C Dating

Willard Libby (1908-1980) won the 1960 Nobel Prize in Chemistry for leading a team that developed the ^{14}C dating method. This technique has had profound implications for determining the age of organic materials that are less than ~50,000 years old. The method is based on measuring the ratio of radioactive carbon to stable carbon in an organic sample. There are three naturally occurring isotopes of carbon: ^{12}C and ^{13}C , which are both stable (i.e., they are not radioactive), and ^{14}C , which is radioactive. Each carbon isotope has six protons in the nucleus, with the number of neutrons varying from 6 to 8 to give the total atomic weight of the isotope ($6+6=12$, $6+7=13$, $6+8=14$).

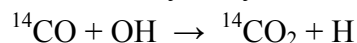
Radioactive ^{14}C is continually produced in the upper atmosphere, mainly by slow neutron bombardment of nitrogen (^{14}N , with 7 protons and 7 neutrons in the nucleus). Energetic particles (cosmic rays) arrive at the Earth's outer atmosphere, where they slam into the nuclei of gas molecules. The nuclei are shattered apart into their constituent neutrons and protons ('spallation' reactions). The free neutrons and protons, which are slower than the original energetic particles, then interact with other atmospheric molecules. For example, a slow neutron from spallation could displace a proton in the nucleus of a ^{14}N atom:



The displaced proton becomes a free atomic hydrogen atom with no neutrons in the nucleus (the hydrogen isotope called protium). The nucleus of the erstwhile nitrogen atom now has one additional neutron, but one less proton. The change in atomic number from losing a proton transforms the nitrogen into carbon, but with the same atomic weight, 14, as the original nitrogen (an isobar). Due to an excess of neutrons in the nucleus, ^{14}C is radioactive with a half-life of ~5730 years (discussed below). The newly formed ^{14}C quickly (<1 day) reacts with oxygen gas to form carbon monoxide (^{14}CO):



The carbon monoxide is then slowly (~2-6 months) oxidized to $^{14}\text{CO}_2$ (carbon dioxide), mainly through reactions with hydroxyl radicals (which are rare in the upper atmosphere, but very reactive):

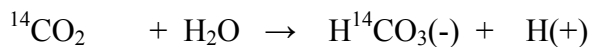


At this point, the $^{14}\text{CO}_2$ slowly (~10-20 years) mixes into all levels of the atmosphere. Of course, there is also $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ mixed throughout the atmosphere as well.

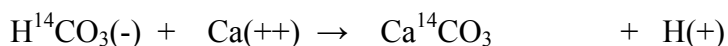
The concentration of CO_2 in the lower atmosphere is currently ~375 ppmV (parts per million volume, or about 0.0375% of atmospheric gases). The lower atmospheric proportions of ^{12}C : ^{13}C : ^{14}C are currently ~0.987:0.013:1.0e-12. These approximate proportions are maintained in the atmosphere by a dynamic equilibrium between production rate and radioactive decay. As a result, the average lower atmospheric ratio of atomic ^{14}C : ^{12}C is approximately 10^{-12} .

Carbon dioxide in the lower atmosphere, including $^{14}\text{CO}_2$, will eventually enter into chemical and physical reactions with other substances at the surface of the Earth. All gases in the lower atmosphere are in kinetic equilibrium with dissolved gases in surface waters. Gases are continually dissolving into, and being released from, surface waters according to prevailing conditions of temperature, pressure and relative equilibrium concentration across the surface. And carbon dioxide in particular may also be removed from the atmosphere by photosynthesis (and returned to the atmosphere by respiration or burning).

Dissolution of carbon dioxide into surface waters creates bicarbonate, which is utilized by many organisms to generate calcium carbonate, as in coral, seashells or bones:

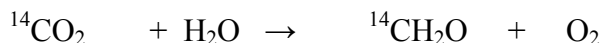


Carbon Dioxide + Water → Bicarbonate + Acid



Bicarbonate + Calcium → Calcium Carbonate + Acid

Once the radioactive ^{14}C becomes part of a coral or bone, it is relatively sequestered from entering into further reactions. Carbon dioxide taken up during photosynthesis is similarly bound up in biomass as carbohydrates:



Carbon Dioxide + Water → Carbohydrates + Oxygen

Cellulose in the trunk and branches of a tree, for example, are formed from carbohydrates produced by photosynthesis. The key point in both of these chemical pathways is that carbon dioxide is the original source of carbon present in the organic products. A small portion of that carbon dioxide contains radioactive ^{14}C that was produced in the upper atmosphere.

If, by chance, a tree, or a shell, or the bone from an animal happens to settle into an environment where it is protected from decay or alteration, then the predictable radioactive properties of the ^{14}C ensconced in the biological material can become the basis of a radiometric ‘clock’ that allows determination of how much time has elapsed since the biological material formed. Like most radioactive elements, ^{14}C undergoes ‘ β -decay’ (sometimes called neutron decay), where a ‘ β -particle’ (an electron or a positron) is emitted. The radioactivity of ^{14}C is due to an excess of neutrons, which causes instability in the nucleus. The weak nuclear force will sporadically convert a neutron into a proton while emitting an electron and an antineutrino:



A neutron in the ^{14}C nucleus decays to a proton, so the ^{14}C atom is transformed into ^{14}N (an isobar) in the reverse manner in which ^{14}C was created from ^{14}N . Radioactive decay of ^{14}C has a half-life of ~5730 years.

Initially, the ratio of $^{14}\text{C}:^{12}\text{C}$ in most biomaterials (e.g., calcium carbonate, cellulose) is on the order of 10^{-12} , close to the average lower atmospheric ratio. But as ^{14}C decays, the $^{14}\text{C}:^{12}\text{C}$ ratio will decrease exponentially, providing the basis for a radiometric ‘clock’. This method assumes that radioactive decay of ^{14}C is the only process that affects the $^{14}\text{C}:^{12}\text{C}$ ratio, which isn’t always true. For example, water seeping into a bone could contain dissolved calcium carbonate. If the bone then dried out, any calcium carbonate dissolved in the water would precipitate inside the bone. The $^{14}\text{C}:^{12}\text{C}$ ratio in the bulk of the bone would be affected, making the bone appear ‘younger’ than it actually is (dissolved calcium carbonate would likely have the average lower atmospheric ratio). In practice, the $^{14}\text{C}:^{12}\text{C}$ ratio (or $^{14}\text{C}:^{13}\text{C}$ ratio) is measured by Accelerator Mass Spectrometry. A sample of the biomaterial is ablated (and ionized), and accelerated through a sensitive mass spectrometer, which counts the relative number of atoms of each weight. Current detection limits are on the order of 10^{-15} , making age estimates beyond ~10 half-lives (~57,300 years) unfeasible.

There is some variability over time in the radiocarbon ratio of the lower atmospheric, due mainly to: (1) changes in Earth’s magnetic field; (2) changes in energetic particle flux impinging upon the outer atmosphere; and (3) reallocation of carbon compounds between various reservoirs of the Earth system (e.g., increased weathering of carbonate sediments, release of carbon compounds from thawing permafrost, increased drawdown of atmospheric CO_2 from expanding phytoplankton populations, degassing of CO_2 from a warming ocean, etc.). Human activity has also affected this ratio in several ways. Atmospheric testing of nuclear weapons nearly doubled the amount of radiocarbon in the

atmosphere in the early 1960s. And the burning of fossil fuels has multiple effects. Fossil fuels are ancient carbohydrates that were converted to hydrocarbons over geological time, and they completely lack ^{14}C due to their great age. As fossil fuels are burned, 'depleted' carbon is released to the atmosphere, affecting the radiocarbon ratio. Burning of fossil fuels also affects the ratio of stable carbon isotopes, because early plants preferentially absorbed light carbon: the 'Suess Effect'. Corrections for variability in the lower atmospheric radiocarbon ratio are generally applied to raw radiocarbon dates. These corrections are available based on analysis of radiocarbon ages from samples of known age, such as dendrochronology of bristlecone pines and other long-lived trees, and analysis of annually laminated ice cores, 'varved' sediments and banded corals. See the references below for more information on calibration of the radiocarbon record.

Some radiocarbon references:

There is an entire journal devoted to ^{14}C : <http://www.radiocarbon.org/>.

An oft-cited article regarding calibration of 'young' radiocarbon ages is:

Stuiver *et al.*, INTCAL98 Radiocarbon Age Calibration, 24,000-0 cal BP, *Radiocarbon*, Volume 40, Number 3, p. 1048 (1998).

INTCAL98 was updated in 2004 to INTCAL04:

P.J. Reimer *et al.*, IntCal04 Terrestrial Radiocarbon Age Calibration, 0–26 cal kyr BP, *Radiocarbon*, Volume 46, Number 3, p. 1029 (2005).

For calibration of 'older' radiocarbon ages:

J. W. Beck *et al.*, Extremely Large Variations of Atmospheric ^{14}C Concentration During the Last Glacial Period, *Science*, Vol 292, Issue 5526, pp. 2453-2458, 29 June 2001.

For a comparison of several calibration data sets over the entire range of radiocarbon ages:

H. Kitagawa and J. van der Plicht, Atmospheric Radiocarbon Calibration to 45,000 yr B.P.: Late Glacial Fluctuations and Cosmogenic Isotope Production, *Science*, Vol. 279, pp. 1187-1190, 20 February 1998.

Two perspectives of Radiocarbon Dating from noted scientists:

E. Bard, *et al.*, A Better Radiocarbon Clock, *Science*, Vol 307, Issue 5655, pp. 178-179, 9 January 2004.

T.P. Guilderson, *et al.*, The Boon and Bane of Radiocarbon Dating, *Science*, Vol 303, Issue 5708, pp. 362-364, 21 January 2005.